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NIR-absorption and NIR-VCD spectroscopy can teach us a lot about OH bonds

Abstract – We briefly review the local mode model and its usefulness to interpret simply and effectively the near infrared absorption and near infrared vibrational circular dichroism spectra (NIR and NIR-VCD respectively). In particular we consider the case of the OH-stretching first overtone region between 6250 and 7700 cm^{-1} (1600 and 1300 nm). With reference and by comparison of newly acquired data for chiral phenylethanol and chiral 2,2,2-trifluorophenylethanol, we show that NIR VCD spectra in that region are quite informative about the OH bond, more than the corresponding fundamental region, between 3000 and 3800 cm^{-1} , which is more accessible to standard instrumentation.

Introduction. The local mode model and NIR spectra

Near-infrared (NIR) vibrational absorption spectroscopy covers the spectroscopic region from straight infrared to the red-visible region (2500-700 nm = 4000-15,000 cm^{-1}): it has been thought generally to be dull and hard to cope with theoretically; for this reason it has been used scarcely in Academia but a lot in industry and for practical reasons, for example in the pharmaceutical industry, agro-food industry, packaging industry and for quality control [1]. The scope of the present chapter is to demonstrate that this spectroscopic region deserves attention also from basic science investigators and can provide useful and fundamental information on molecular structure. This has been recognized for some time, the revived interest dating back to 1980, when considerable progress had been made both experimentally and

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theoretically. Indeed, in the eighties, besides the use of long path-length cells employed in order to be able to detect vibrational features with increasingly lower molecular absorption coefficient at decreasing wavelength [2], several methods were proposed and utilized to investigate also gases, like laser intra-cavity photo-acoustic spectroscopy, thermal lensing, etc. [3-7]. Theoretically, the local mode approximation [2, 8-10] accommodated satisfactorily the interpretation of the many spectroscopic data being accumulated; the local mode model stimulated interested, through a renewed attention to the Morse potential and the alike, also from theoretical physicists utilizing methods, as, e.g. Lie-algebraic methods [11]. The local mode model allows one to approximate the NIR spectrum as the succession of overtone spectra at ν -th order of the uncoupled XH-stretching vibrational modes ($X = C, O, N$, etc.); the large anharmonicity permitting to overcome inter-mode couplings. Concurrently, in the model no combination or mixed mode involving XH-modes plus bath-modes or bending modes is expected to bear intensity, as generally observed.

Our group contributed to the field by testing whether some NIR chiroptical spectroscopy were possible on chiral compounds, and indeed we found it was [12, 13] in the range from 3000 to 600 nm for molecules not containing electronic chromophores, active in the investigated region. Some fifty compounds were studied in our group, in the group of Nafie and in the group of Stephens even earlier [13-15]: for all of them it was possible to measure vibrational circular dichroism (VCD), which has been measured prevalently in the mid-IR range ($3300-1000 \text{ cm}^{-1} \approx 3000-10000 \text{ nm}$). VCD spectroscopy consists in the difference in absorption of left and right circularly polarized light in the IR and NIR range [16]. Theoretically we also contributed to the further elaboration of the local mode model by introducing the effect of *mechanical anharmonicity* and of *electrical anharmonicity* [16-19] in such a way that the new terms are easily computed from ab-initio/DFT quantum mechanical packages [20-21]. In this way, we provided a protocol for calculating the mechanical anharmonicity parameter χ_n together with the harmonic mechanical frequency ω_n for the n -th bond-stretching (or local mode) at ν -th order from the 2nd, 3rd and 4th derivatives K_{nn} , K_{nnn} and K_{nnnn} of the Hessian matrix, to be inserted in the Birge-Sponer or Dunham expansion reported in eq. (1) (all other constants in eq. (1) being easily recognizable fundamental constants):

$$\omega_{n\nu} = hc \left(\omega_n \left(\nu + \frac{1}{2} \right) - \chi_n \left(\nu + \frac{1}{2} \right)^2 \right) \quad \chi_n = \frac{h}{64\pi^2 mc} \left(\frac{5 K_{nnn}^2}{3 K_{nn}^2} - \frac{K_{nnnn}}{K_{nn}} \right) \quad (1)$$

$$\langle \mu_i \rangle_{0\nu} = \sum_{\alpha=H,X} \Pi_{\alpha i z}^0 t_\alpha \langle 0|z|v \rangle + \frac{1}{2} \sum_{\alpha j} \left(\frac{\partial \Pi_{\alpha i z}}{\partial z} \right)_0 t_\alpha \langle 0|z^2|v \rangle + \text{higher - order - terms} \quad (2)$$

$$\langle m_i \rangle_{\nu 0} = \sum_{\alpha=H,C} A_{\alpha i z}^0 \frac{1}{m_R} t_\alpha \langle \nu|p|0 \rangle + \sum_{\alpha=H,C} \left(\frac{\partial A_{\alpha i z}}{\partial z} \right)_0 \frac{1}{m_R} t_\alpha \langle \nu|zp|0 \rangle + \text{higher - order - terms} \quad (3)$$

In eqs. (2) and (3) instead are presented the contributions of electrical anharmonicity to the electric dipole transition moments and magnetic dipole transition moments for the $0 \rightarrow \nu$ transition of the n -th local mode; such contributions are the first derivative of the atomic polar tensor Π and atomic axial tensor A with respect to the n -th XH stretching, involving the α -th atoms (the transition moments just presented enter the dipole strengths and rotational strengths, as for example in refs. [21, 22, and 23]. Explanation of the other constants in eqs. (2) and (3) and generalization to include higher derivatives than the first one may be found in refs. [17, 18 and 19].

Discussion. The first overtone of the OH-stretching region

In this chapter we deal with the first overtone ($\Delta\nu = 2$) of alcohol molecules. For this and even further overtone regions, since just one OH bond is present, the local mode approximation is well justified. Through the method briefly expounded above, we were able to explain the NIR and NIR-VCD spectra of (*R*)- and (*S*)-borneol between 1600 and 1300 nm. [24] The case of borneol is intriguing, since two features are observed for the OH-stretching in NIR-VCD, instead of just one, as observed in the NIR-absorption spectrum and as expected from the local mode model. The explanation we provided in ref. [24] was that three conformers, corresponding to three different orientations of the OH group, are present in solution and VCD is able to detect them, since the sign of VCD is different for one of them with respect to the other two. Thus VCD adds some information, which absorption is unable to pick, since it has got an implicitly higher resolution, due to sign sensitivity. Not only that, the mechanical anharmonicity parameter and mechanical frequency we were able to calculate in ref. [24] are pretty close in value to the ones for ethylene glycol, that Kjaergaard *et al.* [7] had calculated and measured for the OH bond for overtone up to $\nu = 5$, as may be appreciated from Table 1.

Cmpd.	Conformer	$\tau(\text{deg})$	%pop	$\omega(\text{cm}^{-1})$	$\chi(\text{cm}^{-1})$
Borneol (ref. 24)	1-f	68	51.5	3807	88.6
	2-f	174	28.3	3822	86.8
	3-f	300	20.2	3814	90.0
Ethylene glycol (ref. 7)	1-b			3806	82.9
	1-f			3856	84.1

Table 1. Comparison of mechanical harmonic frequencies and anharmonicity constant calculated via DFT for the OH bond in borneol [24] and ethylene glycol [7]. One has three conformers for borneol, for which the OH bond is «free» (f) and several conformers for ethylene glycol, for which the OH bond can be either «free» (f) or involved in a donor-type H-bond (b). Results for just one conformer are provided in the latter case.

The new alcohol-cases that we wish to discuss here are (*R*)- and (*S*)-phenyl ethanol (**1**) and (*R*)- and (*S*)-2,2,2-trifluoro-phenyl ethanol (**2**), differing just in the CH_3 group being substituted by a CF_3 group. In Figure 1 we present the superimposed mid-IR and mid-IR-VCD spectra of both enantiomers of **1** and of **2** in CS_2 and CCl_4 solution respectively (please notice that the VCD spectra of the two enantiomers of the two compounds are opposite, within experimental error). While the data for **2** are from a previous publication of ours [25], the data for **1** are taken from our collection of yet unpublished results.

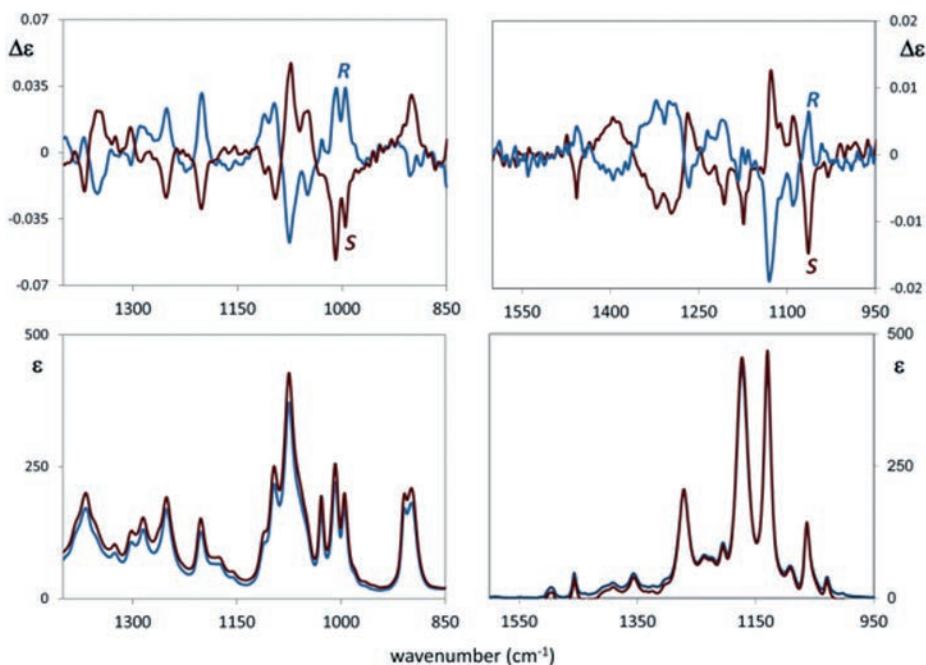


Fig. 1. IR-VCD spectra of phenyl ethanol (**1**) (left) and of 2,2,2-trifluoro-phenyl ethanol (**2**) (right). Spectrum of **1** was recorded in CS_2 solvent at 0.1M concentration in 200 μm cell. Spectrum of **2** was recorded in CCl_4 solvent at ca. 0.1M concentration in 100 μm cell.

We were able to predict [25] the IR and VCD spectra of Figure 1 by DFT calculations carried out by using standard methodology [20, 26]. Computed spectra are not reported here for conciseness. The computed spectra contain fundamental transitions ($\Delta v = 1$) for highly delocalized normal modes resulting from linear combinations of several simple «internal» modes involving CC- and CO- and CF-stretchings and HCC and OH bendings [27]. Besides and more importantly the computed spectra are weighted averages of IR and VCD spectra of different conformers, which are thermally populated through Boltzmann population factors [26]. The conformers

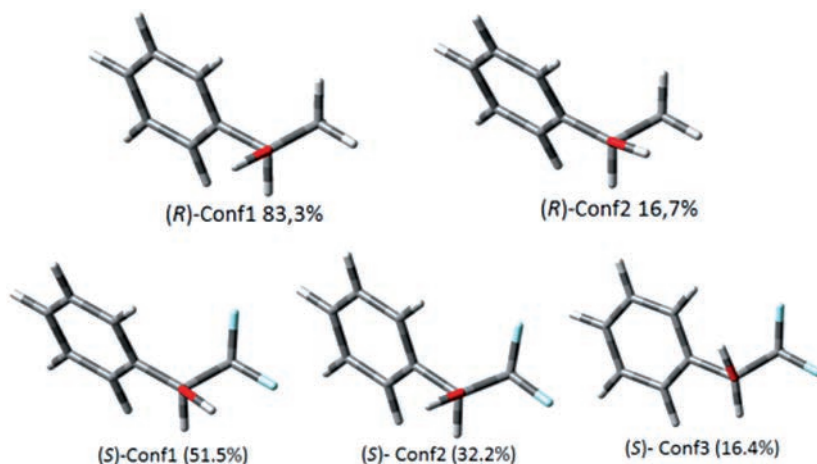


Fig. 2. Calculated conformers of phenyl ethanol (**1**) (first row as *R* configuration) and of 2,2,2-trifluoro-phenyl ethanol (**2**) (second row as *S* configuration). Population factors are reported in brackets.

predicted for these compounds are presented in Figure 2: in the top line one has the conformers for molecule **1** (*(R)*-enantiomer), in the lower line the conformers for molecule **2** (*(S)*-enantiomer).

Please notice that the prevalent conformer for **1** (with a population factor larger than 80%) is such that the positive H atom of the OH bond is strongly attracted by the phenyl moiety. Instead in **2** the OH is pointing to the strongly electro-negative CF_3 -group (with a population larger than 50%), while the conformer with the OH pointing towards PHE is close to 30% in population. This has consequences on the reproduction of the spectra, especially the VCD ones, of Figure 2; however there is no clear, immediately recognizable signature of each one of the two conformers. Instead, a dramatic difference is observed in NIR-VCD spectra of **1** and **2**, which we recorded on our home-made apparatus in the region of the first OH-stretching overtone ($\Delta\nu = 2$) (see Figure 3) on the same solution employed for mid-IR VCD measurements.

The NIR absorption spectrum is very simple and almost coincidental in the two cases, namely it is composed by one single band at ca. 1416 nm with a max absorption coefficient $\varepsilon \approx 1.6 \text{ M}^{-1}\text{cm}^{-1}$, being two order of magnitude lower than in the mid-IR. The NIR-VCD spectrum (which provides mirror-image spectrum for the two enantiomers, as is in the mid-IR) is composed by a single feature in **1** and by a major feature in **2**, accompanied by a minor one at lower energies (longer wavelengths) and opposite sign. The major feature reaches approximately the value $\Delta\varepsilon \approx \pm 1 \times 10^{-4}$ for **1** and the value $\Delta\varepsilon \approx \pm 1.6 \times 10^{-4}$ for **2**, with two orders of magnitude decrease from the fundamental IR stretching region (*cf.* Figure 1). The latter fact, namely that absorption and VCD spectra decrease by similar orders of magnitude at each overtone order has been known for some time, even before the advent

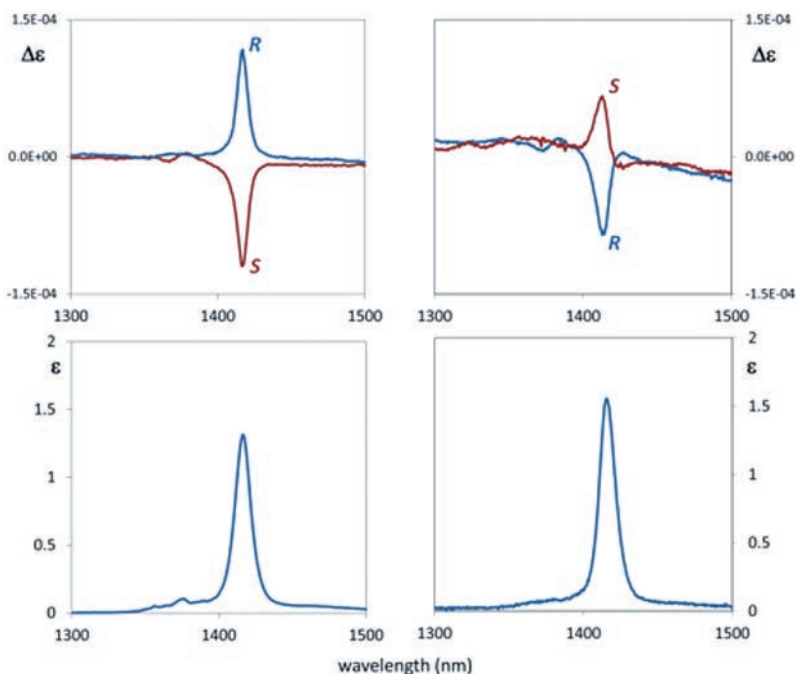


Fig. 3. NIR-VCD spectra of the two enantiomers of phenyl ethanol (**1**) (left) and of 2,2,2-trifluoro-phenyl ethanol (**2**) (right). Spectrum of **1** was recorded in CS_2 solvent at 0.1M concentration in 5 cm quartz cuvette. Spectrum of **2** was recorded in CCl_4 solvent at 0.13 M concentration in 2 cm path-length quartz cuvette.

of DFT calculations [28-30], based on the first extensive application of Van Vleck perturbation theory to the study of VCD anharmonic spectra [31, 32]. However, and most importantly, for the same absolute configuration at the stereogenic carbon, the sign of the major VCD band is reversed. To explain that fact, we first observe that the (C.I.P.) specification of molecular chirality [33] by Cahn, Ingold, and Prelog for **1** is such the groups about the stereogenic carbon C^* are in the decreasing order: OH, Phe, CH_3 , H, while for **2** the order is: OH, CF_3 , Phe, H. Thereby the (*R*) configuration for **1**, as defined by C.I.P. rule, places the chemical groups in the same order as for (*S*)-**2**, once the substitution $\text{CH}_3 \Leftrightarrow \text{CF}_3$ is made (see Figure 2). Moreover, the different conformational properties pointed out above for **1** and **2** give further meaning to what is observed: as it happens in borneol, different orientations of the OH group, are characterized by different signs in the VCD transition. Indeed, as of Figure 2, the conformer prevailing in **1** is quite different from the conformer prevailing in **2**: in the former case OH tends towards the Phe group (# 2 in C.I.P. rule), while in the latter case the OH tends towards CF_3 (once more # 2 in C.I.P. rule). We think that this fact provides physical grounds to the C.I.P. rule and the

NIR-VCD spectrum is directly related to it. In conclusion, the NIR-VCD spectrum is directly related to the local structure of the vibrational chromophore, not only as regards the geometrical characteristics, but also as regards the different electronic chemical environment, through the electrical anharmonicity parameters. The corresponding IR-VCD spectra, examined extensively by Nafie *et al.* [14] for several compounds, is not as informative as the NIR-VCD ones. We finally wish to report that the importance of the first overtone region for the OH-stretching had been pointed out some time ago by Sandorfy *et al.* in seminal studies of NIR absorption spectra of simple alcohols [34].

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